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MOLECULAR SPECTROSCOPY

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COMBUSTION DIAGNOSTICS BY TUNABLE ATOMIC LINE
MOLECULAR SPECTROSCOPY

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I. INTRODUCTION

Considerable effort has been devoted recently towards a detailed understanding of the chemistry of combustion reactions. The difficulty of this task is augmented by the fact that typical combustion processes are often the result of the interaction of physical processes such as heat transfer and molecular diffusion with numerous chemical reactions involving many reactive intermediates. In order to understand combustion at the molecular level, new experimental techniques have been developed for detecting and measuring intermediate and product species formed in combustion processes. Optical techniques are particularly attractive since they provide non-intrusive probes which select atomic or molecular species without disturbing the gas flow field or the chemical reactions taking place.

Although much is known about the combustion chemistry of sulfur containing compounds [1], a basic mechanistic understanding of all of the decomposition and combustion reactions of even relatively simple molecules such as H_2S or CS_2 is not yet available. The principal sulfur containing product formed in the combustion of sulfur compounds is sulfur dioxide (SO_2). In addition to SO_2 , numerous other sulfur containing species are present in flames in significant proportions. Recent experimental laser induced fluorescence measurements of fuel rich $\text{H}_2/\text{O}_2/\text{N}_2$ flames with added H_2S [2] have yielded much information about free radical sulfur species in the post flame gases: SH , S_2 , SO , SO_2 . We present here results on a new optical technique for measuring concentrations of species such as might be present in a flame environment. This technique, called Tunable Atomic Line Molecular Spectroscopy (TALMS), is a line of sight absorption technique which is highly sensitive and selective. Since this technique is based on absorption measurements, interpretation is straightforward and does not require knowledge of collisional quenching and energy transfer rates, as required for quantitative interpretation of laser induced fluorescence experiments. TALMS is based on the Zeeman effect, which allows for magnetic tuning of an atomic line into resonance with a molecular absorption [3]. Atomic absorption spectroscopy based on the Zeeman effect has been used in the analytical determination of atomic species [4] and was recently extended to the detection of small molecules which exhibit sharp rotational electronic structure (e.g. NO [5], SO_2 [6]). We have applied this technique to the detection and measurement of S_2 formed in the equilibrium vapor of elemental sulfur, and from the thermal decomposition of H_2S .

II. EXPERIMENTAL

In the presence of an external magnetic field, atomic energy states which give rise to spectral lines may be split into new states by the Zeeman effect [7]. Transitions between these new states give rise to an emission pattern with components which are not shifted (or shifted slightly) from the zero-field value ν_0 of the transition (the π components), and components which are shifted symmetrically to lower and higher energies about ν_0 (the σ_{\pm} components). Besides differing in frequency, the π and σ_{\pm} components also differ in their polarization.

The splitting of spectral lines produced by the magnetic field as well as the polarization of these lines form the basis for the detection of molecules by Tunable Atomic Line Molecular Spectroscopy. One of the Zeeman components of the atomic emission line is tuned (by varying the strength of the magnetic field) into exact coincidence with a sharp vibrational-rotational transition in the electronic absorption spectrum of the molecule to be detected, while the other component is shifted off resonance. The matching component indicates the extent of absorption by the molecule of interest plus any background absorption due to other species present. The unmatched Zeeman component indicates background absorption only. A differential measurement of the absorption of the matched and unmatched components provides a quantitative measurement of the molecule to be detected.

A block diagram of the experimental apparatus is shown in Figure 1. The light source is a modification of a magnetically confined arc lamp described by Hadeishi and Anderson [8] and is shown in Figure 2.

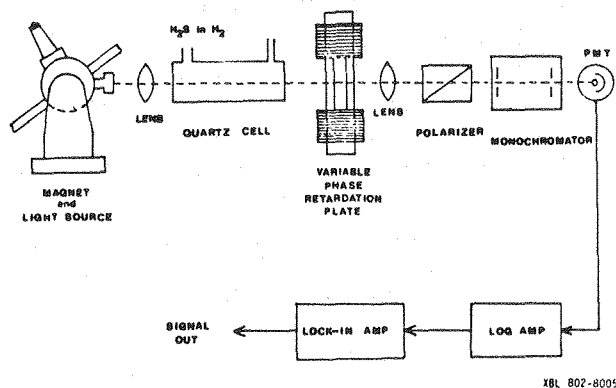


Fig.1: Optical arrangement for the Tunable Atomic Line Molecular Spectrometer.

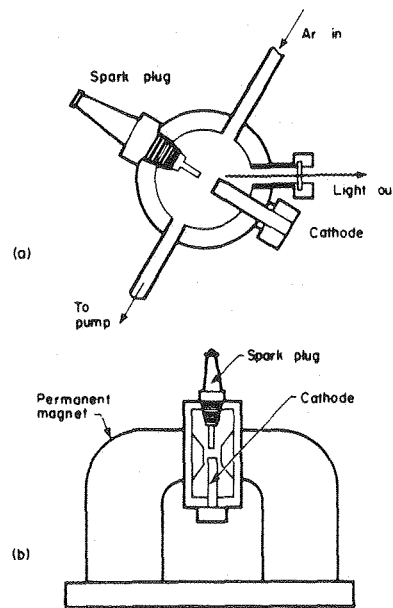


Fig.2: Light source: magnetically confined arc lamp.

The body of the lamp is made from a one inch stainless steel Varian double-sided Conflat flange. Pole pieces made from iron are welded to Conflat flange blanks in order to increase the magnetic field strength at the gap. The cathode is made by spot welding several turns of nichrome tape (Tophet C, 16% Cr, 60% Ni and 24% Fe) to the tip of a stainless steel screw, thus exciting the emission spectra of Ni, Cr, and Fe simultaneously. The anode is constructed from a modified automobile spark plug. Argon gas is flowed through the light source at a pressure of a few torr. A d.c. discharge (30-150 mA) to the cathode results in intense atomic emission, which can be coupled out of the lamp through either a small hole with a suprasil quartz window in one of the pole pieces (for longitudinal observation in a direction parallel to the magnetic field), or through a window in the main body of the lamp (for transverse observation perpendicular to the field). The intensity and stability of the atomic emission are adjusted by varying the pressure in the lamp and the strength of the applied current. A machined boron nitride insert and sheet mica discs are used to prevent arcing to the body of the lamp or to the pole pieces.

The atomic emission is focused through a 24 cm long quartz cell containing a flowing mixture of 10% H₂S in H₂. The gas mixture enters the cell through a 56 cm long quartz side arm. Both the side arm and the absorption cell can be heated to 1000 K. The variable phase retardation plate [9] consists of a block of fused quartz mounted at a 45 degree angle in a magnetic clamp. The stress on the quartz block causes an optoelastic effect and produces a retardation of the phase of the light passing through it. By driving the clamp with an a.c. current, a variable retardation effect is produced, which in combination with the fixed linear polarizer in front of the entrance slits of the monochromator, allows for the alternate transmission of the matched and unmatched Zeeman components of the atomic emission line. The signal is processed electronically and displayed on a strip chart recorder.

III. RESULTS AND DISCUSSION

The electronic spectrum of S₂ has been extensively studied both in absorption and emission [10]. Particular attention has been devoted to the $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ system, which extends from 2500 to 7000 Å and contains hundreds of bands which are resolved into rotational electronic transitions. The emission spectrum of chromium was selected as a good candidate for the detection of S₂, principally because there are several intense atomic lines around 3000 Å, and the emission spectrum was easy to excite in a reasonably stable manner. Furthermore, SO₂, which is the principal sulfur containing product in the combustion of sulfur compounds, absorbs in the region of 3000 Å, and selection of an atomic transition in this region would test the ability to detect S₂ in the presence of SO₂.

Figure 3 shows the differential absorption signal obtained due to the matching of the atomic emission lines with

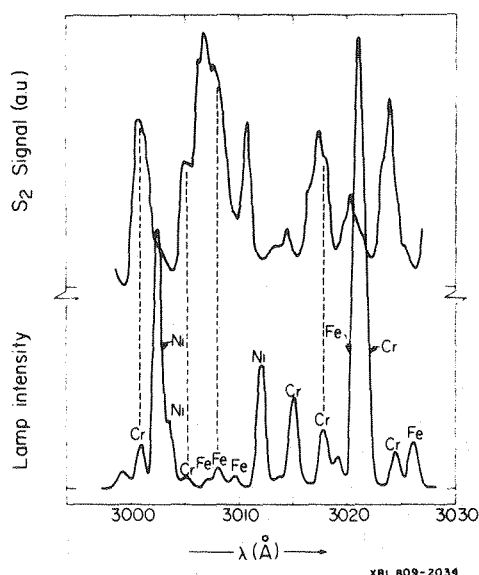


Fig.3: Differential absorption signals due to matching of the Zeeman split atomic lines with molecular absorptions of S₂. H = 5 kG.

individual S₂ molecular absorptions. The lower trace represents a section of the emission spectrum of the nichrome tape (see above), while the upper trace, recorded simultaneously, is the output of the lock-in amplifier. The dotted lines between the two curves show that several atomic emission lines, each one split into its own Zeeman pattern by the external magnetic field, give rise to differential absorption signals corresponding to a match between one of the Zeeman components of each line with a molecular absorption of S₂. Although any one of the matching lines (from Fe or Cr) could be used to detect S₂, we selected the Cr (I) line at 3018 Å because of its higher relative intensity. This Cr (I) emission line was assigned to the transition $5D_3 + 5F_4^0$ at 3017.57 Å (33,129.6 cm⁻¹ vac.) [11].

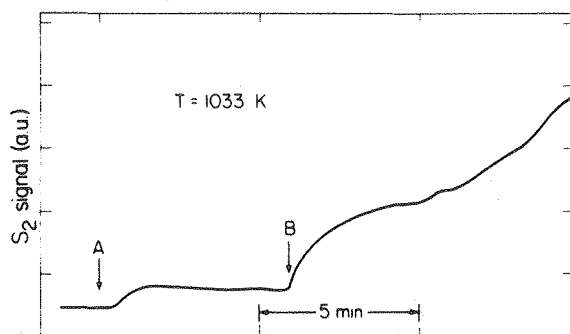
Two different experiments were conducted which demonstrate the high sensitivity and specificity of the TALMS technique. In the first experiment, the 10% H₂S in H₂ gas mixture is flowed through the heated absorption cell. The signal due to S₂ formed by the thermal decomposition of H₂S according to the reaction



is shown in Figure 4. About two minutes after the gas flow is started, the S₂ signal levels off and remains constant for constant flow (~130 standard cc/min). The temperature of the cell is measured with a thermocouple outside the cell, while the temperature of the gas inside the cell is not known, but assumed to be somewhat lower (see below). The concentration of S₂ is proportional to the strength of the differential absorption signal and can be estimated assuming thermodynamic equilibrium for reaction (1). At equilibrium, the S₂ concentration is only a function of the gas temperature. Assuming the gas temperature to be 1000 K, then the calculated equilibrium concentration of S₂ is about 1×10^{-7} atm.

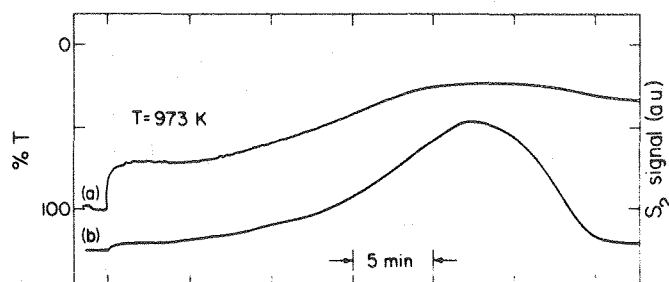
When the flow of the H₂S/H₂ mixture is stopped (point B in figure 4), the S₂ signal increases, probably due to increased formation of S₂ by more effective heating of the gas under no-flow conditions. This increase in the S₂ signal strength is shown in Figure 5(b) on a different scale. Eventually, the S₂ signal decreases as the S₂ disappears from the optical path by reaction or diffusion out of the open cell. Figure 5(a) shows the simultaneous recording of the output of the photomultiplier tube, indicating the extent of absorption by all species present in the heated cell. At the peak of the S₂ absorption signal,

only about 25% of the light is transmitted through the cell. Even after S_2 disappears, the percent transmission remains low, indicating the presence of other absorbing species in the optical path. An UV spectrum of the contents of the cell revealed the presence of SO_2 , which also absorbs in the region from 2900 to 3100 Å. The SO_2 is formed by reaction with atmospheric oxygen backstreaming through the open end of the cell when flow is stopped. Clearly, though, the presence of SO_2 does not interfere with the detection of S_2 .



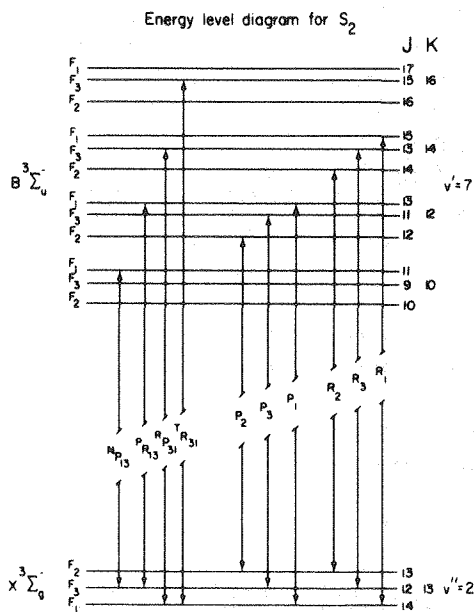
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Fig.4: Signal due to S_2 formed by the decomposition of H_2S (time constant = 25 s).



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Fig.5: (a) Percent transmission through the absorption cell (left ordinate); (b) Differential absorption signal due to S_2 (right ordinate).



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Fig.6: Triplet splitting of the rotational levels of S_2 .

transitions between triplet split levels in the $v'=7 - v''=2$ electronic band of S_2 . Each energy level given by the quantum number K is split into three levels due to the coupling of the rotation of the nuclei with the motion of the electrons [14]. The resulting energy level diagram for $K''=13$ in the (7,2) band of S_2 is shown in Figure 6. The transitions which are allowed between

A different experiment shows the high resolution capability of the TALMS technique [12]. In this experiment, the light source is placed between the poles of an electromagnet, and the flow cell was replaced by a sealed 6 cm quartz cell adapted with a finger containing elemental sulfur, which is heated to produce sulfur vapor. The main body of the cell is heated to 1020 K to insure that all the sulfur vapor is dissociated into S_2 [13].

Differential absorption signals due to S_2 were obtained as a function of magnetic field strength over the range 2-22 kGauss. Two different absorptions were observed corresponding to

these triplet split states are also shown. By scanning the magnetic field, the Zeeman components of the Cr(I) atomic emission line overlapped first the P₃(13) branch of S₂ (calculated at 33,129.7 cm⁻¹), then the weaker satellite branch R_{P31}(21) at 33,130.2 cm⁻¹. Rotational analyses for other (v',v'') bands of S₂ generally resolve only the main P and R branches [15], even with the use of high dispersion (~0.008 Å/mm) vacuum spectrographs. It is remarkable that very high resolution, better than 6 x 10⁴, is possible using the TALMS technique.

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